

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Art Unit : 1745
Examiner :
Serial No. : 10,045,848
Filed : November 7, 2001
Inventors : Hiroki Nakamaru
: Tomoshige Ono
: Yoshiei Kato
Title : IRON POWDER FOR
: REMEDIATION AND METHOD
: FOR REMEDIATING SOIL,
: WATER OR GAS



22469

Confirmation No: 2392

Docket: 1315-01

DECLARATION

I, I. DANIEL CHRISTENBURY, am a resident of 111 E. Lanark Road, Centerville, DE 19807. I am a principal in the firm of Schnader Harrison Segal & Lewis. I am admitted to practice in the States of Virginia and Pennsylvania and am registered to practice before the U.S. Patent and Trademark Office.

The entire complete application, including pages 2, 3, 13, 17 and 19 of the Specification, was deposited in the U.S. Post Office via Express Mail, Certificate No.: EL864966362US for delivery to the United States Patent and Trademark Office under date of November 7, 2001.

I personally checked each page of the entire application and found them all to be present in their entirety and in the correct order, which included aforementioned pages 2, 3, 13, 17 and 19 prior to mailing. This is in accordance with my established regular practice of checking each page of the specification for every application I file in the U.S. Patent and Trademark Office.

I then signed the application papers which were, at that point, placed directly into an Express Mail Envelope and sealed, without disturbing any of the application pages, without removing any of the application papers or disturbing their order. This is possible by virtue of the fact that the file copies and client copies of the Application are made prior to the final checking of the application and determination that all of the application pages are present and in the correct order.

The undersigned declares that all statements made herein of his own knowledge are

true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and thus such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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DECLARATION

I, GINOLA L. JOHNSON, am a resident of 338 Cobble Creek Curve, Newark, DE 19702. I am a secretary in the firm of Schnader Harrison Segal & Lewis.

The entire complete application, including pages 2, 3, 13, 17 and 19 of the Specification, was deposited in the U.S. Post Office via Express Mail, Certificate No.: EL864966362US for delivery to the United States Patent and Trademark Office under date of November 7, 2001.

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New U.S. Application for Hiroki Nakamura et al. entitled IRON POWDER
REMEDIATION AND METHOD FOR REMEDIATING SOIL WITH
GAS

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tion.

J. Daniel Christenbury

[0007] However, in the vapor extraction methods, the pump and treatment facilities and the like, facilities must be separately provided at the site to render the pollutants harmless after the aforementioned drawing or pumping. Therefore, the treatment cost is increased.

[0008] In the methods in which the excavated soil is thermally destructed at high temperatures and the like, a large-scale facility is required for the heat treatment of the soil. Furthermore, since soil particles themselves deteriorate due to heat, and functions of, for example, growing living organisms, which are inherent in the soil, are substantially degraded, it is difficult to reuse the soil after the treatment.

[0009] The bioremediation method cannot be applied to all soil because the soil at each site has different characteristics. Even when it is applied, reactions proceed slowly since they rely on the function of microbes and the method requires a long treatment time and, therefore, has poor usefulness in practice.

[0010] As a method which might overcome the aforementioned problems of conventional measures against the pollutants, various methods, in which halogenated hydrocarbons as pollutants are contacted with iron functioning as a reducing agent to render them harmless by dehalogenation, have been suggested and have attracted attention.

[0011] For example, Japanese Unexamined Patent Application Publication (Tokaihyo) No. 5-501520 (WO 91/08170) describes a method in which a channel is dug in a flow path of groundwater and filled with iron in the form of particles, slices, fibers, or the like.

Subsequently, the iron is contacted with the halogenated hydrocarbons which cause pollution of the groundwater to dehalogenate and render the halogenated hydrocarbons harmless. The iron used in that process is not necessarily specifically prepared and, therefore, generates waste after the process of cutting out is completed and provides such a large pollution, or even a reduction in the steps of cutting iron and the like.

[0012] A method similar to the aforementioned method in which halogenated

hydrocarbons contained in the groundwater as pollutants are rendered harmless by using a metal
iron mixed with activated carbon, is described in Japanese Unexamined Patent Application
Publication (Tokaihyo) No. 6-509631 (WO 92/19556).

[0013] Japanese Unexamined Patent Application Publication (Tokaihyo) No. 11-
235577 discloses a method in which oil- or fat- or organic compounds contained in the soil
above the level of groundwater or the excavated soil is contacted with an iron powder and
rendered harmless by dechlorination. The iron powder used in this method must have a C
content of 0.1% or more and a specific surface area of 0.05 m²/g or more. Further, this iron
powder must have such a particle size that 50% by weight or more of the iron powder passes
through sieve openings of 150µm. A spongy iron ore- reduced iron powder has been
recommended for such an iron powder.

[0014] International Patent Publication WO 97/04868 describes a method in which a
mixed metal produced by precipitating at least one metal selected from the group consisting of
Cu, Co, Ni, Mo, Bi, Sn, Pb, Ag, Cr, Pd, Pt and Au on an iron powder is contacted with an
aqueous composition polluted with halogenated hydrocarbons, and the halogenated
hydrocarbons are dehalogenated and, therefore, the aqueous composition is remedied.

[0015] Each of the aforementioned methods, in which halogenated hydrocarbons as
pollutants are contacted with iron, functioning as a reducing agent and rendered harmless by
dehalogenation, has a certain advantage and, therefore, is superior to conventional measures
against the polluted soil and the polluted groundwater.

[0016] However, the iron used in the aforementioned methods may not be optimized
for the aforementioned purposes and uses and, therefore, there has been a problem in that
halogenated hydrocarbons cannot always be destroyed at a sufficient speed.

[0017] On the other hand, the method disclosed in International Patent Publication
No. 06/76000 is intended to improve the speed of dehalogenation of the halogenated

The media's solubility here may be aerobic or anaerobic. The pH of the media's O_2 is preferably within 1 to 10. When groundwater is remediated, the concentration of dissolved oxygen in the groundwater is not specifically limited and, therefore, the invention can be applied over a wide range.

- 5 [0058] The halogenated hydrocarbons contained in the media's soil, water, and gas undergo a dehalogenation reaction by contact with the iron powder for remediation according to the invention, and are decomposed into harmless compounds containing no halogen elements and hydrogen halides. For example, TCH receives an electron (be reduced) from the surface of the iron powder and forms an unstable intermediate, for example, chloroacetylene, by β elimination. Furthermore, the resulting intermediate is decomposed into compounds not containing chlorine, for example, acetylene. Sometimes, further reactions occur, although at all events, the dehalogenation reaction proceeds by the reception of the electron (be reduced) from the surface of the iron powder and, as a result, decomposition into harmless compounds proceeds.
- 10 [0059] (Examples)

The invention will be described below using Examples, although the invention is not limited to these.

(Examples 1 to 6)

(1) Preparation of iron powder for dehalogenation

- 20 [0060] An as-annealed powder was produced from a molten steel at 1700 °C by a water atomization process. Subsequently, dehydrochlorination was performed in a stream of hydrogen at 900 °C for 1 hour, and then, pulverization and adjustment of particle diameter were performed. The components in the iron powder at this stage were examined with the result that the contents of the primary components, that is, iron contained in the iron powder, were as shown in Table 1.

Table 2

Sample	Iron powder for remediation		Halogenated hydrocarbon destruction test	
	Particle diameter (amount of powder passed through 75 μm sieve) (% by mass)	Metal compound covering rate ¹ (% by area)	Soil	Ground- water
Example 1	60% by mass or more	TiN 5	0.05	0.06
2	60% by mass or more	TiN 10	0.01	0.02
3	60% by mass or more	TiN 30	0.02	0.01
4	60% by mass or more	TiN 60	0.10	0.50
Comparative example 1	60% by mass or more	0	0.99	0.98
Example 5	60% by mass or more	TiO ₂ 5	0.20	0.30
6	60% by mass or more	TiO ₂ 10	0.03	0.05
7	60% by mass or more	TiO ₂ 30	0.02	0.03
8	60% by mass or more	TiO ₂ 60	0.70	0.80
Comparative example 2	60% by mass or more	TiO ₂ 10	0.97	0.98

1) Ratio of TCE concentration of sample to TCE concentration of reference sample after test for 3 days

2) Electric resistivity: TiN $2.17 \times 10^3 \Omega \cdot \text{m}$
 TiO $3 \times 10^3 \Omega \cdot \text{m}$
 TiO₂ $1.2 \times 10^3 \Omega \cdot \text{m}$

(Examples 9 to 12)

[0071] An iron powder for remediation was prepared in a manner similar to those in Examples 1 to 4 by using a V_2O_5 powder (electric resistivity $9.1 \times 10^3 \Omega \cdot \text{m}$) instead of the TiN powder, and the destruction test of the halogenated hydrocarbons in the soil and the destruction test of trichloroethylene in the ground water were carried out. The results are shown in Table 2.

destruction test of the halogenated hydrocarbons in the groundwater were carried out in a manner similar to that in Example 1. The results of the destruction tests and measurements are shown in Table 1.

(Comparative example 2)

- 8 [0074] An iron powder having a TiO_2 powder covering rate of 10% by area was prepared using a TiO_2 powder (electric resistivity $\rho = 1.2 \times 10^6 \Omega \cdot \text{m}$) having an electric resistivity greater than $1 \times 10^7 \Omega \cdot \text{m}$ instead of the TiN powder. Thereafter, the destruction test of the halogenated hydrocarbons in the soil and the destruction test of the halogenated hydrocarbons in the groundwater were carried out in a manner similar to that in Example 1. The results of the destruction tests and measurements are shown in Table 1.

- 10 [0075] When the inorganic compound is not present on the iron powder (Comparative example 1), or the inorganic compound (TiO_2) having an electric resistivity greater than about $1 \times 10^6 \Omega \cdot \text{m}$ is present on the iron powder (Comparative example 2), the speed of destruction is low and, therefore, the trichloroethylene concentrations are hardly decreased after testing for 8 days. On the other hand, decreases in the concentration are clearly observed when an inorganic compound having an electric resistivity of about $1 \times 10^7 \Omega \cdot \text{m}$ or less (TiN: electric resistivity $\rho = 2.17 \times 10^7 \Omega \cdot \text{m}$, TiO_2 : electric resistivity $\rho = 3 \times 10^6 \Omega \cdot \text{m}$, or V_2O_5 : electric resistivity $\rho = 1 \times 10^5 \Omega \cdot \text{m}$) is present on the iron powder for remediation according to the invention (Examples 1 to 12).

- 12 [0076] The iron powder for remediation according to the invention has an unexpectedly and remarkably increased degradation speed of halogenated hydrocarbons. There is no fear of the problem of secondary pollution due to metals contained in the iron powder, and the iron powder of the invention can be inexpensively produced. Furthermore, the iron powder of the invention can be applied to conventional methods, in which iron powder is used to render the pollutants soluble in water and the soluble pollutants are removed